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[Title of the Invention] Process for the Production of a Calcium Carbonate Slurry

[Abstract]

[Problem] To provide a process for the production of a calcium carbonate slurry that has low viscosity and is easy to handle even at a high solids fraction concentration.

[Means of Resolution] A process for the production of a low-viscosity calcium carbonate slurry characterized by adding water-soluble polymer (B) that contains 60-90% by weight of repeating units derived from maleate and/or itaconate, based on the total constituent monomer units, to a calcium carbonate slurry that contains water-soluble polymer (A) having 50-100% by weight of repeating units derived from acrylate, based on the total constituent monomer units, as a dispersant.

[Claim]

[Claim 1] A process for the production of a low-viscosity calcium carbonate slurry characterized by adding water-soluble polymer (B) that contains 60-90% by weight of repeating units derived from maleate and/or itaconate, based on the total constituent monomer units, to a calcium carbonate slurry that contains water-soluble polymer (A) having 50-100% by weight of repeating units derived from acrylate, based on the total constituent monomer units, as a dispersant.

[Detailed Explanation of the Invention]

[0001]

[Industrial Field of Utilization] The present invention relates to a process for the production of a calcium carbonate slurry that has low viscosity and is easy to handle even in a high solids fraction concentration.

[0002]

[Prior Art] Calcium carbonate is widely used in the papermaking and rubber industries, first of all, as well as in plastics, paints, building materials, and agriculture. The use of aqueous slurries of calcium carbonate is increasing in the fields of papermaking and paints because they are easy to handle. The concentration of the calcium carbonate slurry is preferably as high as possible from the standpoints of the transportation efficiency and utilization efficiency. The problem, however, is that the viscosity rises and handling becomes difficult when the concentration is too high.

[0003] Sodium polyacrylate and sodium salts of various copolymers made mainly of acrylic acid such as sodium salts of copolymers of acrylic acid and maleic acid, itaconic acid, methyl acrylate, ethyl acrylate, 2-acrylamide-2-methylpropanesulfonic acid, and styrenesulfonic acid have been used in the past as dispersants to resolve the aforementioned problem. Nonetheless, the high viscosity was still a problem in calcium carbonate slurries with the aforementioned polymers added.

[0004]

[Problems to be Resolved by the Invention] The topic of the present invention is to provide a process for the production of a calcium carbonate slurry that has low viscosity even at a high solids fraction concentration.

[0005]

[Means of Problem Resolution] As a result of in-depth studies conducted to resolve the aforementioned problem, the present inventors discovered that a low-viscosity calcium carbonate slurry that was difficult to obtain by conventional dispersants is obtained by the joint use of two types of specific water-soluble polymers known individually as dispersants for calcium carbonate by the following method and thereby perfected the present invention. Specifically, the present invention is a process for the production of a low-viscosity calcium carbonate slurry

characterized by adding water-soluble polymer (B) that contains 60-90% by weight of repeating units derived from maleate and/or itaconate, based on the total constituent monomer units, to a calcium carbonate slurry that contains water-soluble polymer (A) that contains 50-100% by weight of repeating units derived from acrylate, based on the total constituent monomer units, as a dispersant. The present invention is explained in greater detail below.

[0006]

[Practical Embodiment of the Invention] The water-soluble polymer (A) in the present invention is salt of an acrylic acid homopolymer or copolymer that contains 50-100% by weight of repeating units derived from acrylate. Its weight average molecular weight is preferably 1000-20,000. The weight average molecular weight in the present invention is the value measured by aqueous gel permeation chromatography using sodium polyacrylate as the reference standard.

[0007] Examples of the monomer units that form water-soluble polymer (A) (referred to below as copolymer units) together with the repeating units derived from acrylate include units derived from maleic acid, itaconic acid, methyl (meth)acrylate, ethyl (meth)acrylate), butyl (meth)acrylate, 2-acrylamide-2-methylpropanesulfonic acid, styrenesulfonic acid, acrylamide, and polyalkylene glycol mono(methyl)acrylic acid esters. Two or more types of such copolymer units may be used in combination. Examples of the base that forms the salt in the polymer include sodium hydroxide, potassium hydroxide, ammonium hydroxide, and amines such as alkanolamine and ethylene diamine. Preferred water-soluble polymers (A) are sodium polyacrylate and sodium salts of acrylic acid/maleic acid copolymers (content ratio of maleic acid units 30-50% by weight). The viscosity of the calcium carbonate slurry obtained is high when the proportion of copolymer units in water-soluble polymer (A) exceeds 50% by weight.

[0008] Water-soluble polymer (B) described below is further combined with the calcium carbonate slurry in which the calcium carbonate powder has been dispersed in the water by the aforementioned water-soluble polymer (A) (referred to below as primary slurry). Methods such as dispersing dry-milled calcium carbonate in water in the presence of water-soluble polymer (A), directly dispersing ultrafine light calcium carbonate synthesized by chemical reaction in

water that contains water-soluble polymer (A), and wet-milling calcium carbonate in water that contains water-soluble polymer (A) can be used as the method of producing the primary slurry. The type of calcium carbonate is not particularly restricted and heavy calcium carbonate and light calcium carbonate can be used. The preferred particle diameter of the calcium carbonate is 0.3-1.5 μm for heavy calcium carbonate and 0.1-0.5 μm for light calcium carbonate.

[0009] The proper ratio of calcium carbonate and water in the slurry is 30-70 parts by weight of water per 100 parts by weight of calcium carbonate. The common method of use as a dispersant is used for water-soluble polymer (A). In other words, water-soluble polymer (A) is used in a quantity that makes the viscosity of the primary slurry very low. This quantity differs depending on the type of calcium carbonate and is confirmed by experimentation. It is usually 0.05-1.5 part by weight per 100 parts by weight of calcium carbonate. Examples appear below.

[0010] <Example 1>

Heavy calcium carbonate (wet milled):	100 parts by weight
Water:	30-40 parts by weight
Water-soluble polymer (A):	0.4-1.0 parts by weight

<Example 2>

Light calcium carbonate with a particle diameter of 0.1-0.5 μm:	100 parts by weight
Water:	40-70 parts by weight
Water-soluble polymer (A):	0.6-1.2 parts by weight

[0011] The water-soluble polymer (B) added to the above primary slurry, as mentioned above, is a water-soluble polymer that contains 60-90% by weight of repeating units derived from maleate and/or itaconate (these units are referred to below by the general term bivalent carboxylate units) based on the total constituent units. Its weight average molecular weight is preferably 1000-20,000. Examples of the cations that form the salt in water-soluble polymer (B) include sodium ion, potassium ion, lithium ion, ammonium ion, and cations derived from

amines. The preferred cation in the present invention is the sodium ion. The viscosity of the primary slurry cannot be decreased further when the content ratio of bivalent carboxylate units in the copolymer is less than 60% by weight. On the other hand, polymerization itself becomes difficult and it is difficult to obtain a polymer of the desired molecular weight when it exceeds 90% by weight.

[0012] Examples of comonomers that form water-soluble polymer (B) together with the aforementioned bivalent carboxylate units include α, β-ethylenic unsaturated carboxylic acids such as (meth)acrylic acid, crotonic acid, and fumaric acid and salts thereof; α, β-ethylenic unsaturated sulfonic acids such as 2-acrylamide-2-methylpropanesulfonic acid, styrenesulfonic acid, vinylsulfonic acid, methallylsulfonic acid, and allylsulfonic acid and salts thereof; alkyl (meth)acrylates, polyethylene glycol mono(meth)acrylates, (meth)acrylamide, acrylonitrile, styrene, and vinyl acetate. Preferred comonomers are (meth)acrylic acid and 2-acrylamide-2--methylpropanesulfonic acid or sodium salts of them.

[0013] Water-soluble polymer (B) is usually produced by neutralizing by base a polymer obtained by radical polymerization of comonomers such as maleic acid and/or itaconic acid and (meth)acrylic acid in water or an alcohol-based solvent. A method of adding an aqueous solution of water-soluble polymer (B) directly to the primary slurry is simple as the means of adding water-soluble polymer (B) to the primary slurry. The proper amount of water-soluble polymer (B) to add differs depending on factors such as the type and particle diameter of calcium carbonate in the primary slurry and the slurry concentration. It is decided by the same method as that to decide the amount of water-soluble polymer (A) to use, i.e. by empirical determination of the amount that makes the viscosity of the slurry obtained lowest. Said amount added is usually 0.1-0.3 part by weight per 100 parts by weight of calcium carbonate.

[0014] The present invention is explained more concretely below through practical and comparative examples. Furthermore, % by weight is simply expressed as % below.

[Reference Example 1] 2.5 g of a 40% aqueous solution of sodium polyacrylate (weight average molecular weight 6000) [ratio (solids fraction ratio) to the calcium carbonate 0.1%] and

331.8 g of water were added to 1000 g of commercial dry-milled calcium carbonate (average particle diameter 1.1 μm) and a slurry with a calcium carbonate concentration of 75% was obtained by stirring at 4000 rpm for 10 minutes by autohomomixer (made by Tokushu Kika Kogyo). The viscosity of the slurry obtained (measured by type B viscometer) was 620 cps.

[0015]

[Practical Examples 1-8] Polymers of the monomer compositions and weight average molecular weights shown in Table 1 were added in a solids fraction ratio of 0.05% versus the calcium carbonate to the calcium carbonate slurry obtained in the above Reference Example 1 and stirred at 2000 rpm for 5 minutes by autohomomixer. The viscosity of the calcium carbonate slurries obtained (measured by type B viscometer) was as shown in Table 2. All were less than the starting viscosity of 620 cps shown in Reference Example 1.

[0016]

[Table 1]

Polymer no.	Unsaturated dicarboxylate monomer (%)		Comonomer (%)					Salt form	Average molecular weight
	MLA	ITA	AA	AMPS	NaSS	HEMA	AMD		
(1)	60	—	40	—	—	—	—	Na	4000
(2)	80	—	20	—	—	—	—	Na	5000
(3)	80	—	—	20	—	—	—	Na	5000
(4)	50	20	30	—	—	—	—	Na	6500
(5)	60	—	—	—	20	—	20	ammonium	11,000
(6)	70	—	10	20	—	—	—	Na	7000
(7)	20	40	40	—	—	—	—	Na	5000
(8)	80	—	—	—	—	20	—	K	9800

[0017] The following abbreviations used in Table 1 represent the following compounds.

MLA: maleic acid

ITA: itaconic acid

AA: acrylic acid

AMPS: 2-acrylamide-2-methylpropanesulfonic acid

NaSS: sodium styrenesulfonate

HEMA: 2-hydroxyethyl methacrylate

AMD: acrylamide

[0018]

[Reference Example 2] 618.9 g of water and 22.5 g of the same sodium polyacrylate aqueous solution as was used in Reference Example 1 [ratio (solids fraction ratio) to calcium carbonate 0.5%] were added to 1800 g of calcium carbonate with an average particle diameter of 7.4 μm and wet milled using a sand mill to prepare a slurry with a solids fraction concentration of 74% made from calcium carbonate with an average particle diameter of 1.2 μm. The viscosity of the slurry obtained was 410 cps.

[0019]

[Practical Examples 9-16] The polymers shown in Table 1 were added in a quantity of 0.1% by solids fraction ratio to the calcium carbonate to the calcium carbonate slurry obtained in Reference Example 2 above and stirred for 5 minutes at 2000 rpm by autohomomixer. The viscosity of the calcium carbonate slurries obtained was as shown in Table 2. All were lower than the starting viscosity of 410 cps shown in Reference Example 2.

[0020]

[Table 2]

Practical example	Polymer added	Viscosity (cps)	Practical example	Polymer added	Viscosity (cps)
1	(1)	426	9	(1)	244
2	(2)	510	10	(2)	265
3	(3)	415	11	(3)	302
4	(4)	322	12	(4)	224
5	(5)	450	13	(5)	270
6	(6)	352	14	(6)	248
7	(7)	390	15	(7)	231
8	(8)	468	16	(8)	220

[0021]

[Comparative Example 1] A sodium salt of an acrylic acid/maleic acid copolymer (acrylic acid/maleic acid = 55%: 45%) with a weight average molecular weight of 9500 was added in a quantity of 0.05% by solids fraction ratio versus the calcium carbonate to the calcium carbonate slurry obtained in Reference Example 1 by the same method as in Practical Example 1. The viscosity of the calcium carbonate slurry obtained was 602 cps.

[0022]

[Comparative Example 2] A sodium salt of an acrylic acid/maleic acid/AMPS copolymer (acrylic acid/maleic acid/AMPS = 50%: 20%: 30%) with a weight average molecular weight of 10,000 was added in a quantity of 0.1% by solids fraction ratio versus the calcium carbonate to the calcium carbonate slurry obtained in Reference Example 2 by the same method as in Practical Example 9. The viscosity of the calcium carbonate slurry obtained was 443 cps.

[0023]

[Effects of the Invention] The present invention makes it possible to easily obtain a low-viscosity calcium carbonate slurry not obtained by conventional dispersants.

[Translator's note: The additional bibliographic information that appears at the end of the Japanese patent has been incorporated into the information at the beginning of the English translation.]

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DECLARATION OF ACCURACY AND PRECISION

Re: Translation from Japanese into English

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This declaration certifies the accuracy and precision of the translation from

Japanese into **English**

of the above material and is an accurate rendition of the text as it appeared in Japanese to the translator=s best knowledge and belief.

[For the translator:]

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Translator Date

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